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UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

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Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period from March 3, 2005 to April 3, 2005, under the subject subcontract. The report highlights progress and results obtained under Task 1 (CdTe-based solar cells).

Task 1 – CdTe-based solar cells

High Throughput Processing

Vapor transport (VT) devices are being fabricated with thin CdTe and different back contact processing. The thin CdTe layers are deposited at 550°C in He/O₂ ambient at translation speeds from 2.5 cm/min to 12 cm/min and growth rates from 2-20 microns per min. Table 1 shows best cell results for VT cells made on 2.5 cm x 5 cm pieces cut from 10 cm x 10 cm substrates with CdTe thickness from 1.1 to 1.9 microns and different CdTe surface preparation and contacts. The transparent cells are being developed for bifacial device analysis. The cells were processed using vapor CdCl₂ treatment at 405°C for 15 min. The Bromine-methanol, then Dichromate, then Hydrazine (BDH) process normally used to process cells with 5 micron thick CdTe was found to be too aggressive for cells with thinner CdTe, resulting in severe shunting and low V_{OC}. Improved performance and yield was obtained using aniline treatment followed by CuI deposition and either Ni or graphite (C) contacts, although the fill factor is lower than those of baseline cells. For cells with ~1.5 micron thick CdTe, the data suggests improved uniformity and performance for lower growth rates. The aniline and vapor methods of surface preparation will be further developed to improve yield and performance for cells with both opaque and transparent contacts with nominally 1 micron thick CdTe.

Table 1. Best-cell J-V results for VT cells with thin CdTe absorber layers.

Sample	CdTe Thickness (μm)	Growth Rate ($\mu\text{m}/\text{min}$)	Surface Prep	Back Contact Layer	V _{OC} (mV)	J _{SC} (mA/cm ²)	FF (%)	η (%)
VT139.1A	1.4	18	BrMeOH	CuI/C	563	23	41.4	5.5
VT139.1B	1.4	18	aniline	CuI/C	753	22.7	58.3	9.9
VT139.2	1.4	18	BDH	Cu/Ni	649	23.3	54.1	8.2
VT139.3A	1.4	18	BDH	Cu/Ni	307	19.3	27.3	1.6
VT139.3B	1.4	18	BDH	Cu/Ni	614	23	60.5	8.5
VT139.4	1.4	18	BDH	Cu/Ni	350	19.7	30.5	2.1
VT144.1	1.5	2	aniline	CuI/C	807	25.8	56.8	11.8
VT144.2.1	1.5	2	BDH	ZnTe:Cu	596	21.2	40.3	5.1
VT144.2.2	1.5	2	BDH	ZnTe:Cu	484	21.0	33.0	3.4
VT150.1.1	1.9	9	BDH	ZnTe:Cu	288	14.0	26.9	1.1
VT150.5	1.9	9	aniline	CuI/Ni	774	22.4	53.3	9.2
VT151.1.2	1.1	13	BDH	ZnTe:Cu	249	12.1	27.3	0.8
VT151.3	1.1	13	vapor	CuI/Ni	766	22.7	53.9	9.4

A more detailed analysis of the dependence of performance on thickness was carried out on a single VT sample, in which the thickness was varied over the piece during deposition from 0.75 micron to 1.45 micron. The aniline surface preparation was used in conjunction with a CuI/C contact. Cells were fabricated along the direction of increasing CdTe thickness, as shown in Table 2, which also lists the cell current voltage (JV) parameters and QE at 400 nm, which is indicative of the final CdS film thickness. The CdTe thickness was measured by step profilometry with a Sloan Dektak system.

The V_{OC} decreased and the QE at 400 nm increased with decreasing CdTe thickness, which may indicate more CdS consumption at the thinner side, due to smaller grains and greater CdCl₂ concentration reaching the interface. The QE of the thickest and thinnest cells are shown in Figure 1.

Table 2. Cell performance at different positions corresponding to different CdTe thickness: VT144 processed with aniline treatment and CuI/C contact.

Cell	CdTe Thickness (μm)	QE @ 400 nm	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
2	1.45	0.42	807	25.8	56.8	11.8
4	1.25	0.46	789	25.8	58.0	11.7
6	1.10	0.52	743	23.4	54.8	9.5
8	0.75	0.52	723	22.5	50.5	8.2

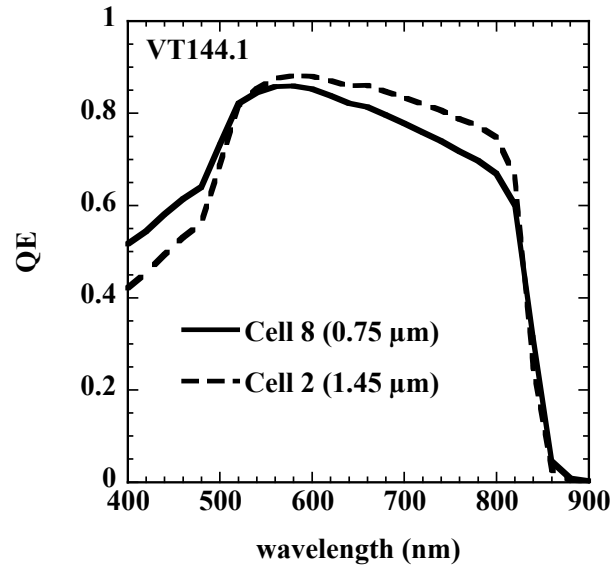


Figure 1. QE versus wavelength of cells 2 and 8, with 1.45 micron and 0.75 micron thick CdTe.

Aniline etched of CdTe

Investigations of aniline-based etching of CdTe have continued. We have previously shown that this treatment, with illumination, produces Te-rich CdTe surfaces. The treatment requires the presence of aniline, acid, Cl ions, dissolved O_2 and consistent illumination, and is proposed to proceed via a photocatalytic-type process where, upon illumination, dissolved aniline is oxidized by photo-generated holes, complemented by reduction of dissolved O_2 to H_2O_2 or similar by conduction band electrons. The generated H_2O_2 , a strong oxidizing agent, is proposed to then react with the CdTe to produce a stable crystalline Te surface. Promising device behavior, exceeding 10% conversion efficiency, has been observed for aniline treated devices completed with Cu-based

back contacts. Here we present the preliminary results of a systematic investigation to determine the optimum aniline treatment conditions for device processing.

Standard aqueous aniline baths containing 0.1 M aniline, 0.01 M *p*-toluenesulfonic acid and 1 M NaCl electrolyte at pH~6.2 were freshly prepared. Samples consisted of ~5 μm thick CdTe films VT deposited on $\text{SnO}_2/\text{glass}$ coated with ~50 nm chemical solution deposited CdS films. The CdTe films had received vapor- CdCl_2 treatment. Aniline-treatments were carried out by illuminating CdTe/CdS samples, immersed in the aniline bath with a 100 W light bulb. The samples were illuminated either directly on the CdTe or through the glass side of the pieces. Devices were processed, following aniline treatment, by applying a Cu-based back contact, completing with a graphite paste secondary contact and annealing for 15 min at 200°C. For comparison, some devices were processed with 10 sec etching in 0.05% $\text{Br}_2/\text{methanol}$ (BM).

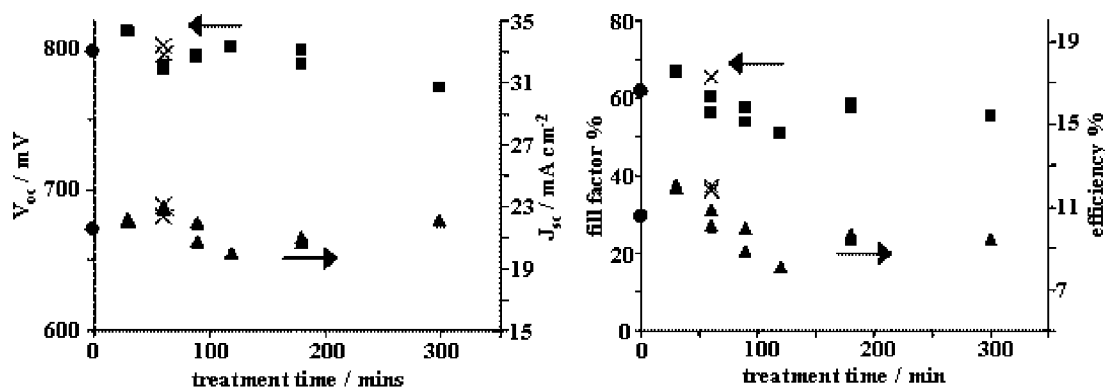


Figure 2. Plots of J-V parameters vs. treatment time for devices processed with the aqueous aniline treatment with illumination either directly on the CdTe (■ and ▲) or on the sample glass (×). Results of devices processed with 10 sec etching in 0.05% BM (●) is shown for comparison.

Figure 2 shows plots of the J-V parameters, V_{OC} , J_{SC} , fill factor (FF) and conversion efficiency (eff) of devices which received aniline treatments over various times, between 30 and 300 min, with illumination directly on the CdTe layer. Plotted for comparison are the J-V parameters of cells processed with a 60 min aniline treatment with illumination on the glass side of the sample and with 10 sec etching in 0.05% BM. The data indicates that very good device performance can be obtained with the aniline etch, with the best devices receiving 30 and 60 min treatments with light on the CdTe and glass, respectively. These devices exhibit V_{OC} ~800 mV, J_{SC} ~23 mA/cm^2 , FF >65% and eff ~12%. The similarity of these two devices suggests that similar surfaces are obtained with the two treatments. At longer treatment times, device performance decreases due to increasing series resistance. After the 300 min treatment, a decrease of V_{OC} to 770 mV was also observed. In comparison the BM etched sample showed comparable performance, V_{OC} ~800 mV, J_{SC} ~21.5 mA/cm^2 , FF =62% and ~11% eff, but exhibited higher series resistance compared to the best aniline etched devices. Despite the slow reaction of the aniline treatment and stability of the generated Te, the best devices are obtained after only relatively short treatment times. This

indicates that the aniline treatment may also affect the CdTe grain boundaries, though the effects are not as harsh or as rapid as can occur during over-treatment with oxidizing etches of CdTe, e.g. BM, $\text{HNO}_3/\text{H}_3\text{PO}_4$, etc. Further optimization of aniline-based treatment of CdTe is under way.

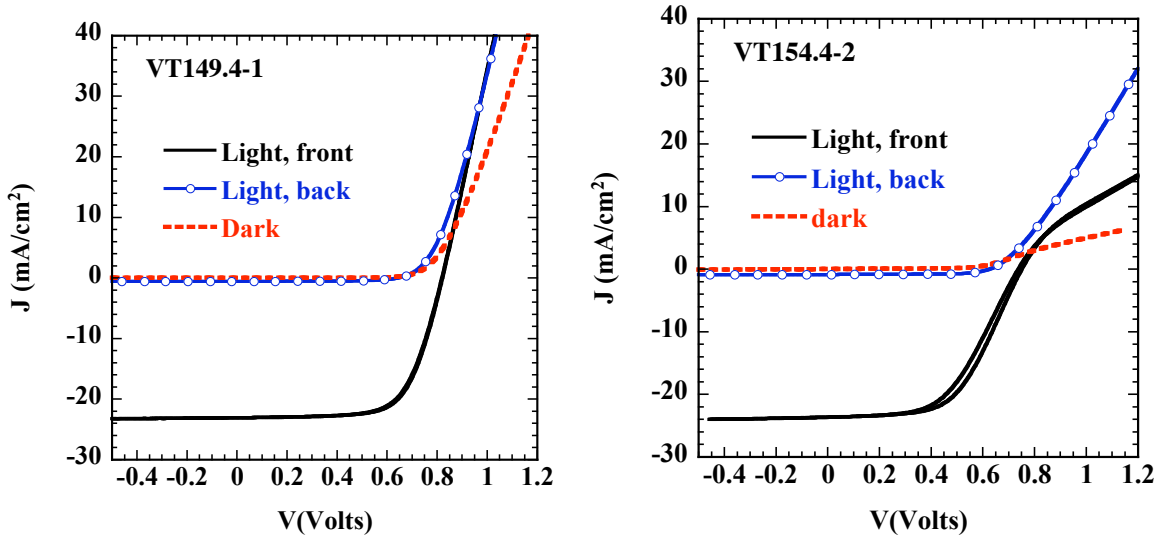
Transparent ZnTe:Cu contacts and bifacial characterization of CdTe solar cells

We have been reporting on the development of Cu-doped ZnTe films grown by galvanic deposition to provide transparent ohmic contacts to CdTe solar cells. Control of the Cu doping with triethanolamine was critical to limit the free Cu in order to achieve high transparency (>60% in the visible) and to minimize shunting. Devices with ZnTe:Cu contacts have comparable performance to devices with standard Cu/Au, Cu/Ni or Cu/graphite contacts. ZnTe:Cu is a promising material for bifacial characterization, as well as tandem cell interconnects and more stable Cu-doped contacts. Some of this information was contained in a poster paper, “Transparent ZnTe:Cu contacts for bifacial characterization of CdTe solar cells” by Darshini Desai, Steven Hegedus, Brian McCandless, and Daniel Ryan, presented at the Spring 2005 MRS conference in San Francisco.

Bifacial J(V) results

ZnTe:Cu films were grown on glass/ SnO_2 /CdS/CdTe substrates. The CdTe was 5 μm thick and was deposited at 550°C by VT at the IEC. The CdTe surface was first etched using the 3-step BDH process to remove any oxide present and create a Te rich surface. The ZnTe:Cu films were grown for 1.5 min with 20 drops of TEA in the solution. Sputtered ITO and evaporated Ni/Al grids were used as secondary back contacts. Figures 3 and 4 show the current voltage (JV) response of recent devices with ZnTe:Cu as a back contact for front wall (through CdS) and backwall (through ZnTe:Cu) illumination.

Figure 3 shows light-to-dark crossover at forward bias, often attributed to Cu-doped photoconductive CdS (PC-CdS), yet the light curve for back illumination shows the same thing. This is not as expected for PC-CdS, since the CdS is “in the dark” for backlight, or for dark measurements. The device in Figure 4 shows rollover (curvature) and high resistance attributed to blocking rear contact. However, the JV curve for the back illumination rises without curvature and has lower resistance. This suggests the back barrier can be photo-modulated. Due to the high absorption of CdTe, the back contact is in the dark for front illumination. We have seen blocking contact curvature, as in Figure 4, on devices from only two of the pieces with ZnTe contacts so far, suggesting that ZnTe:Cu generally makes a lower barrier contact to CdTe. Figure 4 is direct evidence that the back contact barrier is light sensitive.



Figures 3 and 4. Current voltage for light through glass or ZnTe and for dark conditions of a bifacial cell with ZnTe:Cu contact. Both up and down traces are shown.

Table 3 lists the device parameters for the two devices in Figures 3 and 4 as well as for companion pieces receiving standard opaque Cu/Ni contacts. The J_{SC} and V_{OC} are always much lower for back illumination. The reason for the low J_{SC} is evident from the spectral response (SR) curves, discussed in the next section. The lower V_{OC} is largely due to reduced generation, hence J_{SC} , but when the FF for front light is low, the FF for backlight is often much higher, such as for VT154.4. The increase in FF from 55.4%, for front illumination, to 68.2%, for back illumination, in VT154.4 is partially explained by the lower current leading to lower series I^2R loss for back wall JV. In general, ZnTe:Cu contacts typically produce devices with similar front wall performance as compared to standard metal contacts as shown in Table 3.

Table 3. Device results for devices from Figures 3 and 4 with ZnTe:Cu contact for front wall or back wall light and with standard Cu/Ni contacts.

Contact (Sample#)	Light direction	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	Eff (%)
ZnTe(VT149.4)	front	0.82	23.1	68.0	12.9
ZnTe(VT149.4)	back	0.66	0.6	66.3	0.2
Cu/Ni (VT149.1)	front	0.82	23.7	68.7	13.4
ZnTe (VT154.4)	front	0.75	23.7	55.4	9.9
ZnTe (VT154.4)	back	0.64	0.9	68.2	0.4
Cu/Ni (VT154.1)	front	0.80	24.4	60.1	11.8

Bifacial Spectral Response Characterization and Modeling

Bifacial SR measurements are a powerful tool to analyze the transport properties, and to isolate the effect of the front and back junction. A model had been developed previously for bifacial spectral analysis of transparent contact for CIS based photovoltaic devices.¹ This model evaluates the spectral response as a function of absorber thickness (t), depletion width (W) and diffusion length (L). For front illumination, most of the light is absorbed in the depletion region and back junction is in dark. In contrast, for back illumination, most of the light is absorbed in the field free region. Near the back contact, minority carriers must travel a much greater distance to be collected at the front junction. Thus, back illumination should be more sensitive to the diffusion length. A bifacial device provides a tool to study photocurrent collection behavior previously unavailable with front illumination.

Figure 5 shows the front wall and back wall measured and simulated SR. The SnO_2/CdS and ZnTe:Cu absorption is accounted for in the analysis for the front wall and back response, respectively. The measured CdTe absorption coefficient was adjusted slightly to give a good fit to the falling edge of the front wall data. L and W were then fit to the measured back wall response with $L=0.8$ and $W=2.5$ μm . There is good agreement between the measured and fitted data.

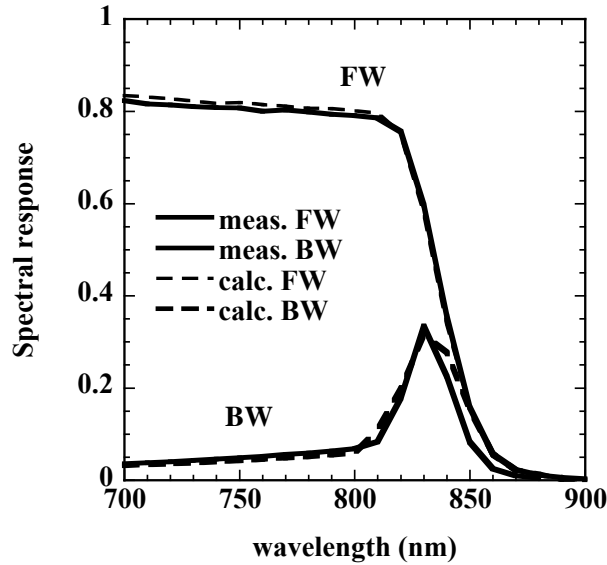


Figure 5. Measured and calculated SR (fit with $W=2.5$ and $L=0.8$ μm).

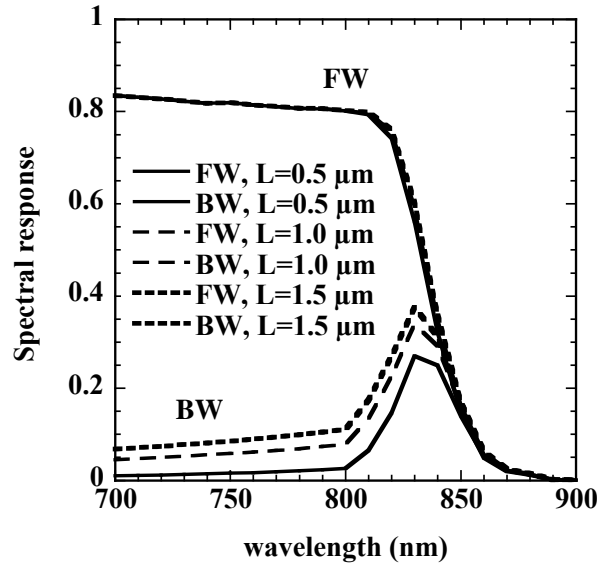


Figure 6. Calculated SR for $L=0.5, 1.0, 1.5$ μm with $W=2.5$ and $t=5.0$ μm .

Due to the extremely high CdTe absorption coefficient and steep absorption edge, over 90% of the photocurrent is generated within the first micron for either illumination direction. For standard front wall measurements, the light is absorbed in the high field depletion regions, leading to very high collection probability independent of t , W or L , providing t and W exceed ~ 1.5 μm . For back wall measurements, most of the electrons generated in the CdTe bulk must diffuse to the CdS junction depletion region. The increasing tail represents this from 400 to 800 nm. Carriers generated in the depletion region by weakly absorbed near-bandgap light (800-860 nm) are

collected with high probability. The peak represents this from 800-860 nm. Typically, we observed very little increase in front wall QE from zero to -1 V bias, indicating good collection and consistent with the strong absorption in the depletion region. The depletion width of $2.5\mu\text{m}$ is very consistent with values obtained by capacitance on these devices, providing independent confirmation of the fitted value. Figure 6 shows the calculated response as function of diffusion length for $W=2.5\mu\text{m}$ and $t=5\mu\text{m}$. The front wall response is insensitive to changes in L but the backwall response shows increased collection at all wavelengths with increasing L . Increasing W primarily increases the collection from 800-860 nm. The back wall SR measurements are much more sensitive to L and W than front wall spectral response.

We intend to perform further experiments with different CdTe layer thickness, to evaluate effects of drift and diffusion on carrier transport. Also, the ZnTe:Cu contact deposited with TEA will allow investigation of the stability of Cu doped contacts. Accelerated stress testing on devices with ZnTe:Cu contacts with different concentrations of Cu is in progress.

Team Activity

Research was carried out under the materials chemistry and device physics subteams. The oxidation study was continued and will be reported at the team meeting in May. Collaboration with the Colorado School of Mines was undertaken to separate the effect on VT devices of CdCl_2 and Cu. The experimental conditions were: fabrication of cells with and without CdCl_2 treatment and with and without intentionally added Cu in contact processing. After JV analysis at IEC, the samples from VT125 were sent to Fred Seymour, Colorado School of Mines, in March for electronic defect measurement. These results will also be reported at the team meeting. Also included in the study were cells fabricated with different O_2 levels. A series of substrates with and without Cu in the contact layer and auxiliary JV and QE data from VT128 were sent to Alan Fahrenbruch, ALF, Redwood City, CA. for transient studies. Results were reported in his MRS paper.

Best regards,

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Director

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¹ J. Phillips, Proc. 21th IEEE Photovoltaic Spec. Conf., 782 (1990).